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The Synthesis and Structure of Stibaindoles

by

Stephen L. Buchwald*, Richard A. Fisher and Bruce M. Foxman

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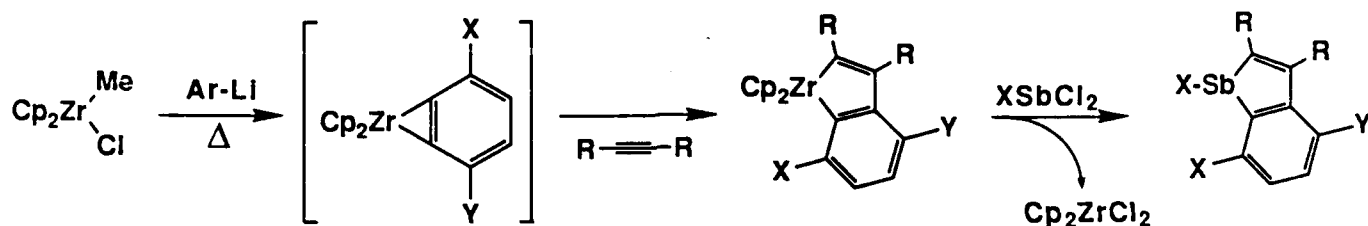
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Recent applications of main group organometallic compounds in the materials sciences has dramatically increased the interest in developing new and more selective synthetic routes to main group organometallic compounds. The first synthesis and structural characterization of a new class of metalloid-heterocycle, stibaindoes, has been accomplished by the application of a transmetallation strategy from zirconium. The facile formation, and ready isolation, of these new compounds bodes well for the role early transition metal complexes may play in the discovery of new and valuable classes of main group compounds.



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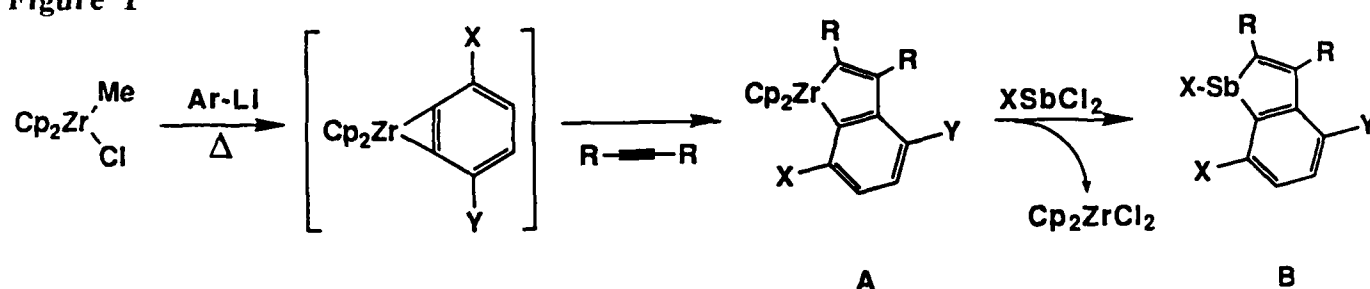
The Synthesis and Structure of Stibaindoles**

By Stephen L. Buchwald,* Richard A. Fisher, and Bruce M. Foxman

Heterocyclic compounds are ubiquitous in organic chemistry and have, consequently, been a popular synthetic target. The vast majority of these efforts have focused on naturally occurring heterocyclic skeletons containing second and third row elements with significantly less attention directed to their heavier main group analogs.^[1] As a consequence, an impressive array of useful reactions is available to the chemist wishing to construct heterocycles of N, O, P, and S, while methods for the synthesis of their heavier analogs are limited.^[2] In this communication, we report the synthesis and characterization of a series of new metalloid-heterocycles, benzo-[b]-stiboles.^[3]

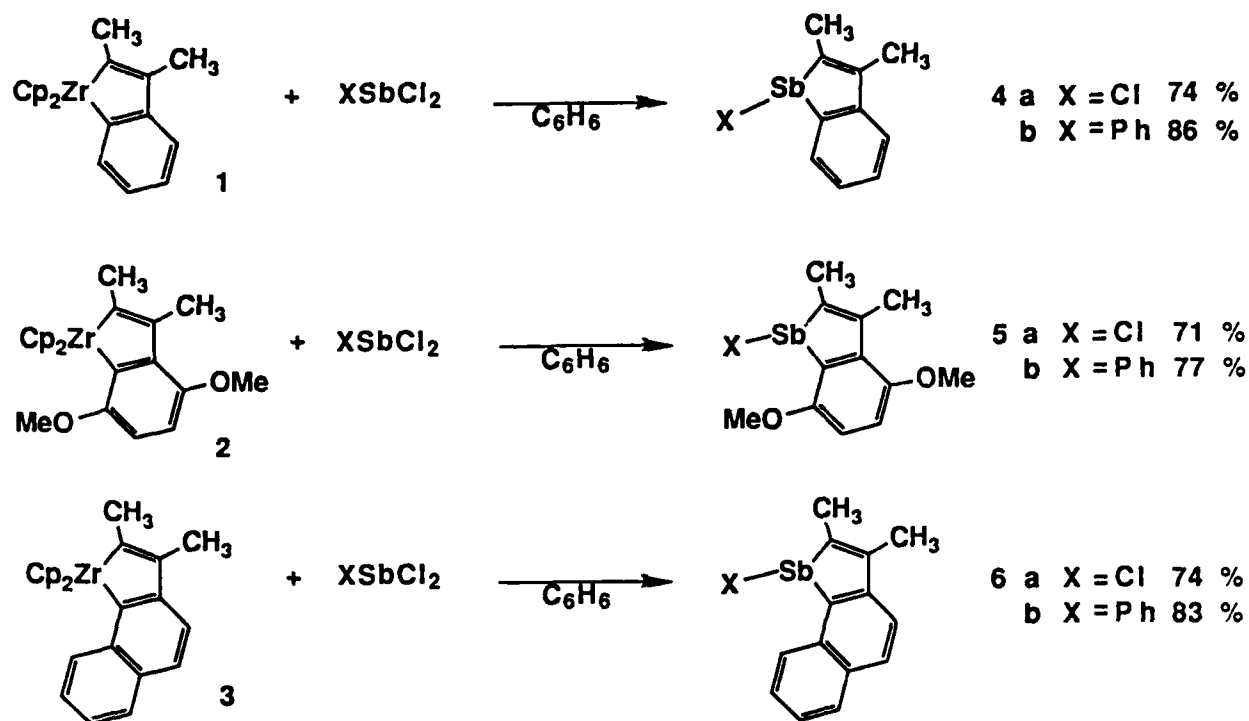
In the course of developing new zirconocene-based methodology for organic synthesis, we,^[4i-k] and others,^[4a-h] have established that sequential treatment of zirconocene(methyl) chloride with an aryl lithium and an alkyne, followed by heating, affords the metallacycle A (Figure 1). The generality of this

Figure 1



reductive coupling reaction is documented elsewhere.^[4] Treatment of benzene solutions of the zirconacycle (A) with one equivalent of XSbCl_2 ($\text{X} = \text{Cl}, \text{Ph}$) produces the benzo-[b]-stiboles (B).^[5] The only byproduct of the reaction, Cp_2ZrCl_2 , is removed by flash chromatography on alumina (III) or MgSO_4 (anhydrous).^[6] Our results are summarized in Figure 2.

Figure 2



The antimony metallacycles (4-6) are moderately air stable, crystalline solids. The 1-chloro derivatives slowly decompose, when stored for prolonged periods in air, to give as yet uncharacterized species. They may be stored indefinitely in a dry nitrogen atmosphere. The 1-phenyl derivatives are substantially more robust and may be stored in the laboratory atmosphere without detectable decomposition. Complexes 4-6 are all considerably more prone to decomposition in solution than in the solid state. All the compounds were characterized by ^1H , ^{13}C NMR, IR, and combustion analysis or HRMS. Solution molecular weight determinations indicate that the stibaindoles are monomeric in benzene solution.^[7]

An X-ray crystal structure determination was carried out on compound **5b**,^[8] and the structure is shown in Figure 3. The stibaindole ring is planar, as anticipated (no deviations greater than 0.03 Å), and orthogonal to the plane of the phenyl ring. The shortest intermolecular Sb-Sb distance is 4.75 Å. The highly pyramidalized geometry about the antimony atom, the bond distances, and bond angles are all in good agreement with other structurally characterized stibole derivatives.^[9]

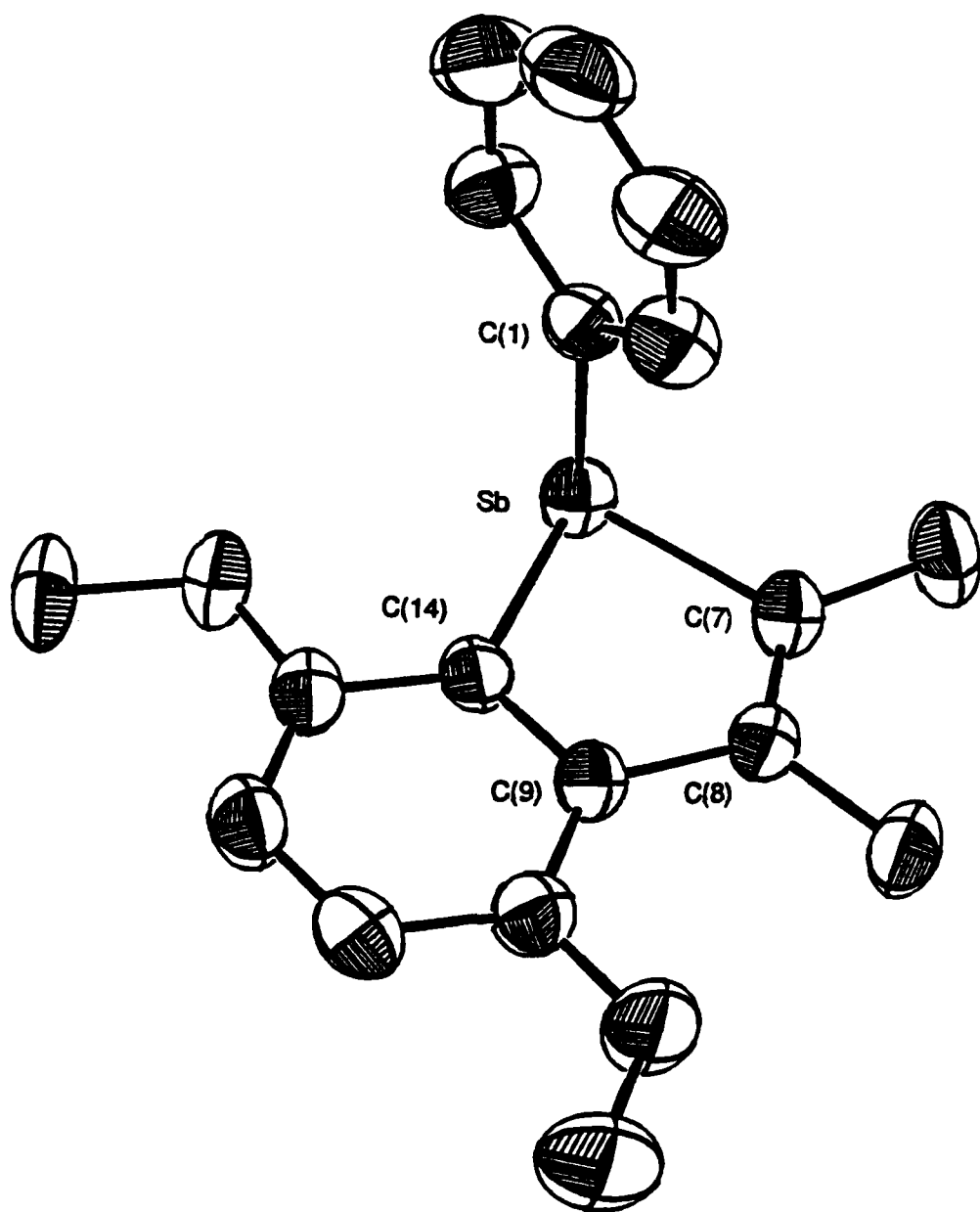
Figure 3

Molecular structure of **5b**. Bond Distances (Å): Sb-C1, 2.164(4); Sb-C7, 2.131(3); Sb-C14, 2.119(3); C7-C8, 1.334(4); C8-C9, 1.504(3); C9-C14, 1.387(4). Angles(°): C1-Sb-C7, 96.5(1); C1-Sb-C14, 95.5(1); C7-Sb-C14, 79.9(1).

Continued interest in heterocyclic compounds coupled with recent applications of main group organometallics in materials science provides a powerful incentive for the development of new and more selective synthetic routes to main group metallacycles. Results from this laboratory, and elsewhere, indicate that early transition metal complexes may play an important role in the discovery of new and valuable classes of main group compounds. Further investigations of the synthesis, reactivity and determination of the properties of other main group metallacycles are ongoing in our laboratory.

Experimental:

General procedure the preparation of Stibaindoles: The zirconacycle (1.00 mmol) was dissolved in 20 mL benzene in a nitrogen filled dry box. Either antimony trichloride (0.228 g, 1.00 mmol) or phenylantimony dichloride (0.270 g, 1.00 mmol), was added, all at once, as a solid. After 5 minutes, the flask was sealed with a septum, brought out of the dry box, and the solvent removed, *in vacuo*, on a Schlenk line. Zirconocene dichloride and the desired stibaindoles were the only species detectable in the crude reaction mixture as determined by ^1H NMR. The zirconocene dichloride was separated from the product by extraction with 10/1 hexanes/ether followed by rapid chromatography on either anhydrous MgSO_4 (**4a**, **5a**, **6a**) or alumina III (**4b**, **5b**, **6b**).



Footnotes and References:

- [*] Prof. Stephen L. Buchwald,
Richard A. Fisher
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
- Prof. Bruce M. Foxman
Department of Chemistry
Brandeis University
Waltham, Massachusetts 02254
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